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ON THE EFFECTS OF CERTAIN INACTIVE SUBSTANCES ON THE OPTICAL ACTIVITY OF PINENE

By

CHARLES BALDWIN GATES

A Thesis Submitted for the Degree of
MASTER OF PHILOSOPHY

UNIVERSITY OF WISCONSIN
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ON THE EFFECTS OF CERTAIN INACTIVE SUBSTANCES ON THE OPTICAL ACTIVITY OF PINENE

The object of this work was to find what substances, or classes of substances, would dissolve in pinene, yielding clear solutions, sufficiently light in color to permit their being used in the polariscope; and then to determine the specific rotation of the solutions thus formed. The rotation of the pure solvent being known, comparable results were obtained, which it was hoped might throw some light on the question of solution itself.

The solutions were made up carefully, each component being weighed out to the fourth decimal place. The specific gravity (D_4^{25}) was determined at once, with the same degree of accuracy. Then the solution was put into a two-decimetre tube and its rotation determined immediately, that there might be as little opportunity for slow change as possible. For pinene itself, a six-decimetre tube was

used to secure greater exactness, and the shorter tube employed only as a check. A current of water at 25°C. was kept continually flowing through the jacket of the tubes and the rotation determined at that temperature.

The specific rotation was calculated from the formula,-

$$(\alpha)^{25}_{D} = \frac{100 \cdot \alpha^{25}_{D}}{l \cdot p \cdot d},$$

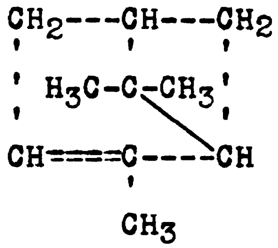
where α^{25}_{D} was the actual rotation observed; l, the length of the tube in decimetres; p, the number of grams of solvent to every 100 grams of solution; and d, the density of the solution.

The polariscope was one made by Franz Schmidt and Haensch, of Berlin. The scale could be read to the third decimal place, but I found that the third figure had no significance. Usually a set of readings would agree to within four units in the second place. Such a series, taken at random, is given below.

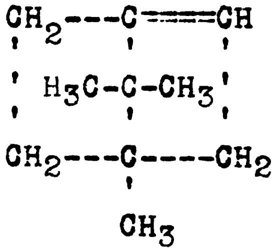
247.934
.955
.937
.932 Average- 247.942
.923
.965
.945

The error is thus seen to be small,- not more than plus or minus two units in the second decimal place. I have carried none of my results farther than this.

Pinene itself is one of the terpenes and probably has the constitution represented by the formula,(1)



Chemically pure pinene, as prepared by Wallach,(2) is optically inactive. The optically active varieties have a specific gravity of 0.8587 to 0.8600, and a rotatory power, $(\alpha)_D = +32^\circ$ to $(\alpha)_D = -43^\circ 4$.(3) If Wagner's structural formula is the correct one, we might expect pure pinene to be inactive, for there is no regular asymmetric carbon atom. It must be remembered, however, that asymmetry does not depend necessarily on the immediate connections of the carbon, but may depend on more remote connections, as in the case of menthene and limonene.(4) Ordinarily, pinene may have some other molecular arrangement. At least two others have been suggested;-



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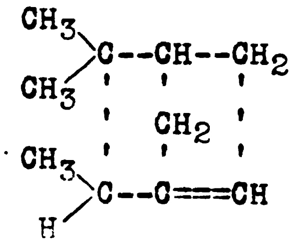


(6)

American, Russian and German turpentine oils yield dextrorotatory pinene, French oil mostly the laevorotatory variety. The rotations vary widely, according to the source and preparation of the hydrocarbon.

To prepare my pinene, ordinary commercial turpentine oil was shaken up with a five percent solution of caustic potash and then three-fourths of the original amount distilled off with steam and run through a separating funnel. It was then distilled by itself, and the fraction coming over between 155°- 157° C. kept. This fraction was redistilled and only the first three-fourths of the distillate used. The results of the various preparations are shown in table 1.

The final product was kept from the air and light as much as possible, to prevent rapid oxidation to pinene glycol, $C_{10}H_{16}(OH)_2$ and keto-alcohol, $C_{10}H_{16}O_2$. (7) As it was, changes did occur, as is shown in the second table.

TABLE 1.

	1st Batch	2nd Batch	3rd Batch
1st Distillation	156°.5-158°.5 bar.= 76.55 (23°.2)	155°-157° bar.= 73.65 (22°.0)	155°-157° bar.= 73.4 (17°.0)
2nd Distillation	155°.0-158°.0 bar.= 74.3 (21°.5)	155°-157° bar.= 73.65 (22°.0)	155°-157° bar.= 74.0 (19°.0)
D_4^{25}	0.8548	0.8575	0.8576
$(\alpha)_D^{25}$	+ 18°.29	+ 18°.11	+ 17°.43

TABLE 2.

Batch	D_4^{25}	$(\alpha)_D^{25}$	
2nd	0.8575	+18.11	Original product
	0.8598	+18.12	After four weeks
3rd	0.8576	+17.43	Original product
	0.8588	+17.47	After three weeks
	0.8598	+17.49	" five "

The first class of substances to be dissolved in pinene were the oleates. Besides the liquids, pure oleic acid and glyceryl oleate (refined cotton-seed oil), four metallic oleates were prepared. The general method followed was to mix the calculated amounts of oleic acid and caustic soda, so as to get a neutral sodium oleate solution. This was diluted to several hundred times its volume, allowed to come to room temperature (the cooler the better), and the calculated amount of metallic sulphate solution slowly added. A very finely-divided precipitate of the metallic oleate resulted. None of these precipitates could be washed on filters, because of their tendency to cake into sticky masses, which could not be handled. So they were allowed to settle slowly in a large volume of water and then the clear liquid above was siphoned off and fresh water added. This washing was continued until no traces of sulphate were found in the water drawn off, even when boiled with barium chloride and allowed to stand over night. The oleates were then roughly dried on filter paper and finally in an air-bath, between 120° 140° C.

These oleates were very sparingly soluble in pinene, giving, on the average, only about one percent solutions. Their optical behavior was tested by dissolving

TABLE 3.

Solute	Solute		D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
	%	M. Wt.				
$Zn(C_{18}H_{33}O_2)_2$	1.01	627.93	0.8616	+18.34	+0.05	
Ba(" $)_2$	1.01	699.93	0.8601	+18.75	+0.46	Equal % of oleates
Pb(" $)_2$	1.01	769.43	0.8611	+18.19	-0.10	
H (")	0.99	282.27	0.8584	+18.30	+0.01	
Al(" $)_3$	0.001	870.89	0.8584	+18.67	+0.38	Pinene
Mg(" $)_2$	0.53	586.89	0.8592	+18.33	+0.04	" + 18.29

them in benzene and they were found to be entirely inactive. Table 3 shows the results when equal weights of oleates were dissolved in a constant weight of pinene.

As is seen, the aluminum and magnesium solutions have less oleates in them than the other four, yet the rotation is of the same general order. It would seem from this that the percentage strength of the solution has but little relation to the general rotatory effect. The same thing will be more strikingly illustrated later. Oleic acid had only a very slight effect and this small increase is within the limits of possible experimental error.

Then chemically equivalent quantities of the oleates were dissolved and the same general increase of rotation found. Table 4.

TABLE 4.

Solute	Solute		D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
	%	M. Wt.				
$Ba(C_{18}H_{33}O_2)_2$	0.597	699.93	0.8600	+18.34	+0.23	Chemically equivalent quantities of oleates.
$Mg($ " $)_2$	0.501	586.89	0.8586	+18.21	+0.10	
$Zn($ " $)_2$	0.535	627.93	0.8593	+18.27	+0.16	
$Pb($ " $)_2$	0.655	769.43	0.8597	+18.18	+0.07	Pinene
$H($ " $)$	0.242	282.27	0.8576	+18.17	+0.06	"
						+18.11

Lastly, the oleates were dissolved in such quantities that the percentage amount of oleic radical in each solution might be constant. That is, the amounts of oleates dissolved were proportional to their molecular weights, divided by the number of oleic radicals in each salt. This would give a series of solutions with one ($C_{17}H_{33}COO$) group each, but with varying weights of Zn, C_3H_5, H and Ba.

TABLE 5.

Solute	Solute %	 M. Wt.	D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
$Zn(C_{18}H_{33}O_2)_2$	0.49	627.93	0.8608	+17.52	+0.05	Equivalent quantities of oleic radicals.
$C_3H_5($ " $)_3$	0.461	883.92	0.8594	+17.54	+0.07	
H (")	0.441	282.27	0.8592	+17.53	+0.06	
$Ba($ " $)_2$	0.546	699.93	0.8606	+18.24	+0.77	Pinene = +17.47

As will be seen from a comparison of tables 4 and 5, where different batches of pinene are used, the amount of rotational increase for solutions of nearly equal strength, may vary quite considerably. However, the change is always an increase and sufficiently large to be well beyond the limit of experimental error.

Four metallic abietates were then prepared in the same way as the oleates, from abietic acid, a monobasic compound of the formula $C_{20}H_{30}O_2$, as determined by Kremers and Mead. This particular acid had been prepared from Oregon balsam and crystallized from glacial acetic acid by Dr. Kremers. The abietates, too, were found to be optically inactive when dissolved in benzene.

Table 6 shows that these abietates all have the same qualitative rotational effect on pinene and it is to be noted that it is just the opposite of what the oleates showed.

TABLE 6.

Solute	Solute %	Solute M. Wt.	D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
$Mg(C_{20}H_{29}O_2)_2$	1.706	626.82	0.8617	+17.51	-0.60	Equivalent quantities of abietates.
$Ba($ " $)_2$	2.007	739.86	0.8642	+17.86	-0.25	
$Zn($ " $)_2$	1.816	667.86	0.8636	+17.72	-0.39	
$Pb($ " $)_2$	0.544	809.36	0.8630	+17.64	-0.47	Pinene= +18.11

TABLE 7.

	Oleates		Abietates	
	Mol. Wt.	Change of rot.	Mol. Wt.	Change of rot.
H	282.27	+0.06		
Mg	586.89	+0.10	626.82	-0.60
Zn	627.93	+0.16	667.86	-0.39
Ba	699.93	+0.23	739.86	-0.25

A rather curious relation exists between the rotations and the molecular weights of the substances in tables 4 and 6. If the lead salts be disregarded, it will be seen from table 7 that as the molecular weight of the oleates increases, the rotation also increases, though not in the same ratio. In the case of the abietates, the negative change of rotation decreases.

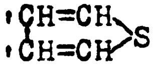
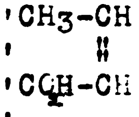
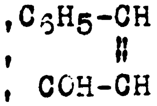
This would seem to indicate that there is some relation between the weight of the solute involved and the effect on the rotatory power of the solvent. But the increase in molecular weight is due to the different metallic elements, in so far as these are united to equal numbers of acid radicals. This is true of the magnesium, barium and zinc oleates and abietates, where the divalent metal is in all cases combined with two of the oleic or abietic radicals. The relation, if there is any, must exist,then,between the atomic weights of the metals and the rotation produced. But in one set of salts these metals increase the rotation, and in the other, decrease it. If the rotations were comparable quantitatively, the qualitative change of sign would have to be attributed to the radical-end of the salt. This is true of the barium salts only and probably is a mere coincidence here.

The whole salt must be concerned in producing

the change,- not the metallic element alone. It may be that these salts form addition products, which shift the center of gravity of the asymmetric, tetrahedral,carbon group in some manner proportional to the molecular weights of the salts themselves. For a discussion of this theory of asymmetry, the reader is referred to the work of Guye.(8)

Why lead does not conform to the rule is not clear. It is probably true that these apparent exceptions are due to the inherent characteristics of these salts. As far as our knowledge goes now, that is all that can be said regarding their peculiar behavior. They were as carefully prepared as the others. The lead abietate was soluble to the extent of about one-fourth the amount calculated to make it comparable with the other three and even then its deviation from its theoretical position in the series is marked.

TABLE 8.

Solute	Solute		D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
	%	M. Wt.				
$C_3H_5(OH)_3$	7.10	92.06	0.8561	+19.44	+1.33	
C_5H_5N	6.16	79.08	0.8631	+18.11	+0.00	
$C_6H_5NO_2$	9.27	123.08	0.8817	+18.40	+0.29	Pinene
$C_{10}H_8$	9.61	128.06	0.8714	+17.98	-0.13	"
CS_2	5.94	76.12	0.8748	+18.04	-0.07	+18.11
CCl_4	11.32	153.80	0.9063	+18.16	+0.05	
PCl_3	10.24	137.35	0.9114	+16.93	-1.18	
$(CH_3)_2CO$	4.60	58.05	0.8548	+18.38	+0.26	Pinene
C_2H_5SH	4.90	62.11	0.8579	+18.25	+0.13	"
CH_3COCl	6.12	78.47	0. 875	+17.56	-0.56	+18.12
$C_{10}H_{20}O$	11.48	156.16	0.8629	+18.15	+0.03	
$CHCl_3$	9.01	119.36	0.8905	+17.85	+0.42	
$C_2H_4Br_2$	13.50	187.95	0.9283	+17.54	+0.11	
CH_3COOH	4.75	60.03	0.8620	+17.80	+0.37	
CH_3COOCH_3	5.79	74.06	0.8586	+17.86	+0.43	Pinene
$(C_3H_7)_2NH$	7.75	101.16	0.8466	+17.65	+0.22	"
CH_3OH	2.59	32.03	0.8543	+17.67	+0.24	+17.43
C_2H_5OH	2.95	46.05	0.8544	+17.56	+0.13	
$C_6H_5CHCl_2$	9.60	160.95	0.8842	+17.52	+0.09	
CCl_3COOH	9.72	163.36	0.9056	+15.32	-2.11	
	6.52	84.09	0.8679	+17.34	-0.09	
	6.67	86.05	0.8659	+17.80	+0.37	Pinene " +17.43
	9.88	132.06	0.8733	+17.66	+0.23	
$S=C=N-C_6H_5$	9.41	125.14	0.8793	+17.31	-0.12	

In table 8, a large number of very diverse substances have been dissolved in pinene in chemically equivalent quantities; that is, in quantities proportional to their molecular weights. Pyridine seems to have had no effect, which was noticable. Glycerin gives the greatest increase and tri-chlor-acetic acid the greatest decrease. I tried to get a stronger solution of the latter, but the color was too deeply red to permit its rotation being found. Seven percent of glycerin is nearly the strongest solution that can be obtained. It is only miscible with pinene to a limited extent and if more glycerin is added, two layers appear.

Menthol is optically active itself. When prepared from peppermint oil, $(\alpha)_D = -59^\circ$ (9) Yet even when eleven percent of it was present, it increased the positive rotation of pinene. This fact would be difficult to explain, if the solution is looked upon as a simple mechanical mixture. It points toward a chemical union of some kind, the resulting combination having a different optical activity from either of the components. A few unsaturated compounds were dissolved in pinene, but had comparatively little effect. See oleic acid and the last four substances in the preceding table.

TABLE 9.

Solute	Solute		D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks	
	%	M. Wt.					Pinene
$FeCl_3$	0.34	162.25	0.8596	+17.06	-0.37		+17.43
I	0.25	126.85	0.8594	+17.38	-0.15	Equivalent	+17.43
Br	0.16	79.96	0.8652	+17.78	+0.29		+17.49
Br	7.88	"	0.9098	+15.45	-1.98		+17.43

The compounds in table 9 gave highly colored solutions and so were not made equivalent to those in the preceding group. When iodine was put into pinene, chemical action was manifested by a violent effervescence and heat. Fumes of hydriodic acid were given off and the solution became dark-red in color. On heating, the color suddenly changed to yellow,- the iodine entering into combination with the solvent. Bromine acted much the same, but combined even more violently. This element yielded a slightly yellow solution at once.

Evidently, substitution, and not addition products, are formed in these two cases. It is to be noted how marked is the difference between the effects of iodine and bromine, the two halogens even giving a change of sign. The difference in chemical activity of the two will not account for this variation. The relatively less active iodine might seem only to decrease the specific rotation of pinene, because it decreases the observed rotation. But there is no doubt whatever that a marked chemical reaction took place during the process of solution. The iodine was not present simply as a dilutant of the pinene.

When bromine was present in much larger quantity, its effect was strongly negative, as the table shows.

It should be remembered that various complications arise here, due to the presence of hydrobromic acid in the bromine, even before it is dissolved in pinene. This unites with pinene as well as the pure bromine. Inactive $C_{10}H_{16}HBr$ (10) is formed along with the solid dibromide, $C_{10}H_{16}Br_2$, which is dextro-active. Iodine may act similarly and so the final rotation is the resultant of several factors. No definite conclusions can be drawn from these data. For a discussion of the formation of addition and substitution products of bromine with pinene, see the work of Wallach, Oppenheim and Tilden. (11)

TABLE 10.

Solute	Solute %	Solute M. Wt	D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
C_5H_5N	50.00	79.08	0.9098	+18.05	-0.06	Pinene= +18.11
CS_2	50.00	76.12	1.0186	+17.00	-1.11	50% solutions.

TABLE 11.

Solute	Solute %	Solute M. Wt	D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
C_5H_5N	50.00	79.08	0.8900	+19.02	+0.90	Pinene= + 18.12
CH_3COCH_3	25.00	58.05				
CS_2	50.00	76.12	0.9805	+18.06	-0.06	Three components.
CH_3COCH_3	25.00	58.05				

Both pyridine and carbon bisulphide were tried in fifty percent solutions of pinene. The increase in the percentage of pyridine seems to be accompanied by a very small decrease of dextro-activity. See table 8. On the other hand, an increase in the percentage of carbon bisulphide is accompanied by a very considerable decrease of activity.

By comparing tables 10 and 11, it would seem that acetone has a strong tendency toward increase of the normal activity of pinene, when present in large quantities. The strongly negative action of carbon bisulphide accounts for the negative change of rotation in the table above. To determine whether carefully prepared acetone does have this effect, some,specially dried and distilled, was made up into a fifty percent solution. The same thing was done with carbon tetrachloride, which had shown a very small increase in table 8. The results are given below.

TABLE 12.

Solute	Solute %	Solute M. Wt	D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
CH_3COCH_3	50.00	58.05	0.8172	+19.69	+2.20	Pinene= +17.49
CCl_4	50.00	153.8	1.1106	+18.09	+0.60	50% solutions.

TABLE 13.

Solute	Solute %	Solute M. Wt	D_4^{25}	$(\alpha)_D^{25}$	Effect on (α)	Remarks
CS_2	75.00	76.12	1.1025	+16.42	-1.07	Pinene= +17.49
C_5H_5N	75.00	79.08	0.9410	+17.88	+0.39	
CH_3COCH_3	75.00	58.05	0.7988	+21.01	+3.52	75% solutions.

Table 13 gives three seventy-five percent solutions. Carbon bisulphide has not changed much from the fifty percent solution, while pyridine has become quite positive in its action. Acetone has increased very much.

As acetone gave such a remarkable increase of rotation, several,more concentrated solutions were tested. All the work on acetone is given in the following table.

TABLE 14.

% Pinene	% Acetone	D_4^{25}	$(\alpha)_D^{25}$	Change of rotat.	Rotation of pinene
95.4	4.6	0.8548	+ 18.38	+ 0.26	+ 18.12
50.0	50.0	0.8172	+ 19.69	+ 2.20	+ 17.49
25.0	75.0	0.7988	+ 21.01	+ 3.52	+ "
5.0	95.0	0.7865	+ 21.59	+ 4.10	+ "
2.0	98.0	0.7858	+ 21.82	+ 4.33	+ "

The actual angles observed constantly grew less, but not so rapidly as did the corresponding concentrations of pinene. And so it happens that the specific rotation increases and is greatest when there is the least amount of the active component present. The accompanying curve shows the increase of rotation with increase of acetone. See page 27.

Biot (12) noticed this effect of varying concentration on the rotation of solutions of turpentine. He stated that the values of specific rotation, calculated from work on solutions, are more or less variable numbers, for, as Landolt puts it, "the molecules of the active substances seem to suffer some alteration by the presence of the inactive solvent particles".(13) Other work on the variability of specific rotation with concentration has been done by Oudemans (14) and Hesse.(15)

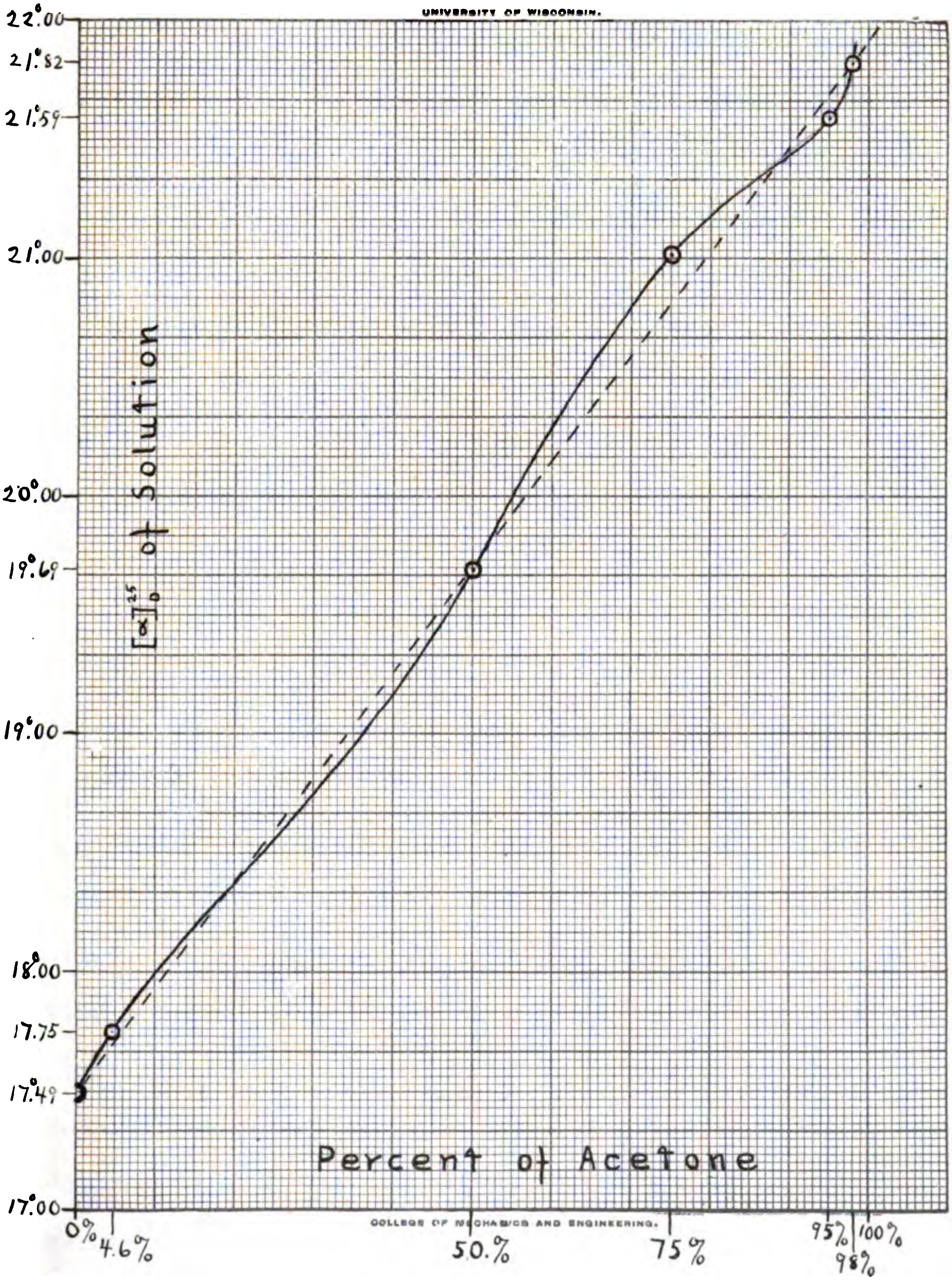
To find the real value of the rotation, the equation of the curve may be solved. If it is a straight line, as it is approximately in this case,

$$(\alpha)=A+Bq$$

where q is the percentage amount of solvent and A and B the constants of the curve.

If it is part of a parabola or hyperbola,

$$(\alpha)=A+B_q+Cq^2$$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If q is zero, on solving for (α), we get the specific rotation of the pure active substance. If q is 100, the equation gives the specific rotation of a solution of infinite dilution. If we assume that the active body has entirely disappeared,- where $q=100$, $(\alpha)=0$. Biot has worked out the derivation and application of these curve equations.(16)

The interesting thing about these data is the relatively great activity of pinene in strong acetone solution,compared to its activity in such other solvents as carbon tetrachloride, carbon bisulphide and pyridine.

The effects of drying agents were tried on pinene itself and are tabulated on the next page. None of these three chemicals went into solution, as far as could be discovered. After a piece of caustic soda had been standing in pinene for thirty-six hours, ten cubic centimetres of the liquid were evaporated on a watch-glass and no residue remained. Then the rest of the pinene was shaken up with water and the water tested with red litmus paper, with no better result. One drop of normal hydrochloric acid immediately changed the color of the indicator in eight cubic centimetres of the above water. Caustic soda is the only one of the three that seems to affect the rotation. If this

TABLE 15.

(α) of pure pinene	Substance in contact	D_4^{25}	$(\alpha)_D^{25}$	Change of rotat.
+18.12	NaOH - 24 hours	0.8590	+18.20	+0.08
+18.12	Na_2CO_3 - 4 hours	0.8601	+18.11	-0.01
+17.43	$CaCl_2$ - 2 hours	0.8579	+17.41	-0.02
+17.43	NaOH - 36 hours	0.8576	+17.52	+0.09

change is due to the abstraction of a small quantity of water, it is difficult to see why calcium chloride should not have had a similar effect on the same pinene. It must be borne in mind, however, that there is a difference in the attraction of these two substances for moisture.

Quite a number of substances were tried with pinene, but refused to yield workable solutions. Among them were: -

Antimony trichloride	-	chemical action	- cloudy, mixture.
Arsenic "	-	" "	- precipitate, white.
Stannic chloride	-	" "	- precipitate, dark-brown.
Sulphuric acid	-	" "	- deep red solution.
Nitric acid	-	" "	- same.
Butylamine	- -	" "	- cloudy mixture.
Pyrrol	-	" "	- same.

Do not dissolve -

Abietic acid
Phthalic anhydride
Silver nitrate
Starch
Copper sulphate
Potassium cyanide
Pyrogallol
Potassium permanganate
Mercuric chloride
Potassium bromide
Oxalic acid
Picric acid
Phenol
Chloral hydrate

Sodium oleate
Lithium chloride
Cinnamic acid
Stannous chloride
Mercuric bromide
Lithium citrate

Do not mix with pinene —

Acetic acid anhydride
Formic acid
Acetonitrile
Mono-chlor-acetic ether
Hydrochloric acid
Di-chlor-acetic acid
Furfurol

A little over sixty percent of the substances that did go into solution produced an increase of rotation. None of them, save menthol, are optically active themselves. I can see no other explanation of the result than that the solvent is no longer present as pure pinene. Loose chemical combinations have taken place, giving a resulting complex of still higher dextro-rotatory power than has pinene itself. The chemical union is no doubt a very weak one, but it results in a combination which has a definite rotation. If a little more solute is added, the weak affinities readjust themselves, a new product is formed, and a new rotation results. Optical activity is a definite property of certain substances, depending upon definite molecular configuration. When the rotation increases, it would seem to indicate some

change in connection with the asymmetric carbon atom. Possibly addition products are formed by the breaking down of the double bond of the terpene. In some cases, substitution evidently took place, as when hydriodic and hydrobromic acids were evolved.

The other forty percent produced a decrease of rotation. If these substances simply diluted the pinene, there ought to have been no change of specific rotation; for being inactive themselves, they would simply diminish the volume of active pinene. This would mean a smaller actual rotation, but the concentration (d . p) of the pinene would be diminished at the same time and in the same ratio, and therefore the quotient of these two would remain constant and the specific rotation would not be changed. But as the rotation does change, these substances that cause the decrease cannot be present as mere mechanical dilutants.

Nothing very definite can be stated as to the actual condition of affairs, until the whole problem of solution has been worked out more fully. Such investigations as these have a direct bearing on the problem of solutions. They lead us toward the conclusion that solutions are not mixtures, but rather loose chemical combinations, taking place according to variable proportions.

References

1) Wagner, Ber., 27, 1636,(1894).

2) Wallach, Ann. Chem., 252, 132,(1889); 258, 343,(1890).

3) Kannonikow, Ber., (1881), 1697.

4) Landolt, Optical Rotation of Organic Bodies. Tran. by Long, p. 48.

5) Bredt, Ber., 26, 3047,(1893).

6) Tiemann and Semmler, Ber., 29, 3027,(1896).

7) G. Wagner, Ber., 27, 2270,(1894).

8) Guye, Compt. rend., 110, 714,(1890); 111, 745, (1890); 114, 473,(1892): 116, 1133, 1378, 1451, 1454,(1893): 119, 906,(1894): 120, 157, 452, 632, 1274,(1895). Ann. CHIM. Phys. (6), 25, 145,(1892).

   Guye and Chavanne, Compt. rend., 116, 1454,(1895): 119, 906,(1894).

9) Chemistry of the Terpenes, Heusler-Pond, p. 309.

10) Wallach and Conrady, Ann. Chem.(Liebig), 252, 156, (1889).

11) Wallach, Ann. Chem., 264, 1,(1891).

    Oppenheim, Ber., 5, 94 and 627,(1872).

    Tilden, Journ. Chem. Soc., (1888), 882; 69,(1896), 1009; Ber., 22, 135,(1889).

12) Biot, Ann. Chim. Phys.,(3), 36, 257,(1852).

13) Landolt, See reference 4, p. 169.

14) Oudemans, Pogg. Ann., 148, 337,(1873): Ann. Chem., 166, 65,(1873).

15) Hesse, Ann. Chem. (Liebig), 176, 89, 189,(1875).

16) Biot, Ann. Chim. Phys., (3), 11, 96,(1844); 10, 399, (1844); 59, 224,(1860).

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L. Kahlenberg.

C. F. Burgess.

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